

PATENT ABSTRACTS OF JAPAN

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(71)Applicant : MATSUSHITA ELECTRIC IND CO LTD

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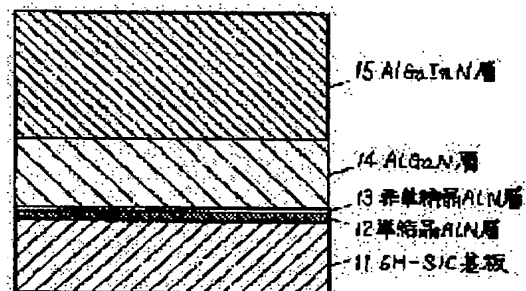
(72)Inventor : MANNOU MASAYA
ONAKA SEIJI

(54) SEMICONDUCTOR THIN FILM AND MANUFACTURE THEREOF

(57)Abstract:

PURPOSE: To provide a method for forming a high-quality AlGaInN thin film which has only a small amount of dislocation and point defects and which is suitable for manufacturing a blue semiconductor laser element which can be used for a blue light emitting diode, etc.

CONSTITUTION: This is a method for forming an AlGaInN thin film on the surface of a heated SiC substrate through a buffer layer by supplying material including group III elements and material including nitrogen. First of all, a single-crystal AlN film 12 is formed on an SiC substrate which is heated to 800° C. Then, a non-single-crystal AlN layer of 20nm in thickness 13 is formed at a substrate temperature of 600° C. Next, a single-crystal AlGaInN layer 14 is formed at a substrate temperature of 900° C or above. Then, a lattice matching AlGaInN layer 15 is formed on the AlGaInN layer 14. By this method, the appearance of a dislocation and point defects is prevented and thereby a high-quality AlGaInN thin film can be formed.



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CLAIMS

[Claim(s)]

[Claim 1] It is the approach of supplying the raw material containing the raw material containing an III group configuration element, and nitrogen, and forming an AlGaInN thin film through a buffer coat on the heated substrate front face. The process which forms the buffer coat which consists of AlGaIn after forming the first AlGaIn single crystal thin film on said substrate. Subsequently, the manufacture approach of the AlGaInN semi-conductor thin film characterized by including the process which forms an AlGaInN single crystal thin film after forming the second AlGaIn single crystal thin film.

[Claim 2] It is the approach of supplying the raw material containing the raw material containing an III group configuration element, and nitrogen, and forming an AlGaInN thin film through a buffer coat on the heated substrate front face. The process which forms the buffer coat which consists of AlGaIn after forming the first AlGaIn single crystal thin film on said substrate. Subsequently, the process which forms the strained layer superlattice structure which consists of an AlGaInN layer from which two or more presentations differ in said second AlGaIn single crystal thin film and on said second AlGaIn single crystal thin film after forming the second AlGaIn single crystal thin film, ***** — the manufacture approach of the AlGaInN semi-conductor thin film characterized by things.

[Claim 3] It is the manufacture approach of claim 1st characterized by forming the first and second AlGaIn single crystal thin films at the substrate temperature of 800 degrees C or more, and forming the buffer coat which consists of AlGaIn at the substrate temperature of 800 degrees C or less, or an AlGaInN semi-conductor thin film given in 2.

[Claim 4] The manufacture approach of the AlGaInN semi-conductor thin film according to claim 1 or 2 characterized by making into 300 or more revolutions per minute rotational speed of the heating object which the approach of forming is the vapor growth using an organic metal, and has arranged the substrate.

[Claim 5] The manufacture approach of the AlGaInN semi-conductor thin film according to claim 1 or 2 characterized by a substrate being SiC or ZnO.

[Claim 6] The semi-conductor diaphragm structure characterized by having a single crystal AlGaIn layer, the buffer coat which consists of AlGaIn formed on said single crystal AlGaIn layer, and the AlGaInN layer formed on the buffer coat which consists of said AlGaIn.

[Claim 7] The semi-conductor light emitting device characterized by depositing a semi-conductor diaphragm structure according to claim 6 on a SiC substrate or a ZnO substrate.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates [the blue which can be used for the light source for information processors, such as green / blue light emitting diode and an optical disk, or] to thin film formation of a nitride system ingredient especially about the manufacture approach of the semiconductor laser component of short wavelength further.

[0002]

[Description of the Prior Art] Since 670nm band AlGaInP system red semiconductor laser was commercialized in 1988, development of short wavelength semiconductor laser has been actively performed as the light sources for information processors, such as a laser beam printer and an optical disk. Although 670-690nm was the core of development at the beginning, a wavelength field is shifting to helium-Ne gas laser and 630nm band of this level with the demand of an improvement of the visibility of a bar code reader, the densification of an optical disk, etc. Furthermore, it will be further anxious for implementation of the semiconductor laser ranging from the blue and green to an ultraviolet area of short wavelength from red with increase of storage capacity in the future, and research of II-VI group system semiconductor laser has been progressing quickly ignited by p mold conductivity-type control having been attained. On the other hand, although gallium nitride (GaN) was an ingredient promising as a light emitting device ranging from the blue to an ultraviolet region in the compound semiconductor of a direct transition mold with about 3.4eV extensive energy gap, since a GaN bulk substrate crystal could not produce easily and there was no suitable substrate crystal for others, the development as semiconductor laser was seldom progressing.

[0003] as the production approach of a GaN thin film — an alpha-aluminum 2O3 (sapphire) substrate top — MOVPE — generally the approach of carrying out vapor growth by law (metal-organic chemical vapor deposition) is used. It is going to decompose, and this tends to make trimethylgallium and ammonia react on the front face of the substrate heated at about 1050 degrees C, for example, silicon on sapphire, and tends to grow a GaN thin film. Using C (0001) side of sapphire, it was proved that a comparatively good GaN thin film could be formed through GaN and the AlN buffer coat which were deposited at low temperature, and it was commercialized as blue light emitting diode, and resulted in until recently.

[0004]

[Problem(s) to be Solved by the Invention] According to the above-mentioned conventional technique, since the difference of the very big grid mismatching of 13.8% or a big coefficient of thermal expansion was between a sapphire C side and GaN, a pit and a crack tended to go into the grown-up nitride, it was uniform, and growth of the good nitride of surface smoothness was difficult.

[0005] When the buffer coat deposited at low temperature was minded, relaxation of grid mismatching was started efficiently, although growth of the nitride of mirror plane nature was possible, two or more [108cm -] misfit rearrangements still existed, and formation of a quality thin film was difficult [it is flat, and]. Furthermore, according to the conventional technique, since sapphire was used as a substrate, there was a problem that processing was difficult and production of a device was not easy.

[0006] This invention aims at a rearrangement offering the formation approach of few good AlGaInN thin films of surface smoothness. It aims at providing coincidence with the formation approach of the quality AlGaInN thin film to the easy substrate top of processing.

[0007]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, the formation approach of an AlGaInN thin film according to claim 1 In the approach of supplying the raw material containing the raw material containing an III group configuration element, and nitrogen, and forming an AlGaInN thin film through a buffer coat on the heated substrate front face It is characterized by including at least the process which forms the buffer coat which consists of AlGaIn after forming the first AlGaIn single crystal thin film on said substrate, and the process which forms an AlGaInN single crystal thin film after forming the second AlGaIn single crystal thin film subsequently. As for the buffer coat which forms the said first and second AlGaIn single crystal thin films at the substrate temperature of 800 degrees C or more, and consists of said AlGaIn here, it is desirable to consider as the substrate temperature of 800 degrees C or less.

[0008] The formation approach of an AlGaInN thin film according to claim 2 In the approach of supplying the raw material containing the raw material containing an III group configuration element, and nitrogen, and forming an AlGaInN thin film through a buffer coat on the heated substrate front face The process which forms the buffer coat which consists of AlGaIn after forming the first AlGaIn single crystal thin film on said substrate, Subsequently, the process which forms an AlGaInN single crystal thin film after forming the second AlGaIn single crystal thin film, It is characterized by ***** which includes at least the process which forms the strained layer superlattice structure which consists of an AlGaInN layer

from which two or more presentations differ in said second AlGaIn single crystal thin film and on said second AlGaIn single crystal thin film. As for the buffer coat which forms the said first and second AlGaIn single crystal thin films at the substrate temperature of 800 degrees C or more, and consists of said AlGaIn here, it is desirable to consider as the substrate temperature of 800 degrees C or less.

[0009] As for making into 300 or more revolutions per minute rotational speed of the heating object which has arranged the substrate, and a substrate, in the above claim, it is desirable that they are SiC and ZnO.

[0010]

[Function] According to the production approach of the AlGaInN thin film of claim 1, there are the following operations.

[0011] When a grid mismatching difference and a coefficient-of-thermal-expansion difference with AlGaInN use very small SiC and a ZnO substrate compared with silicon on sapphire, if it is below critical thickness, a single crystal AlN thin film can be deposited on flat and homogeneity. Since the non-single crystal AlN deposited at low temperature on this AlN thin film is deposited on the single crystal which consists of the same element, that front face becomes possible [flatness and supposing that it is uniform].

[0012] Furthermore, since the non-single crystal buffer coat is deposited at low temperature through a single crystal layer, the impurity diffusion from a substrate can be reduced remarkably. Therefore, compared with the AlGaInN layer deposited only through the non-single crystal buffer coat on conventional silicon on sapphire, propagation of the defect generated from the buffer coat interface is reduced remarkably, and can reduce sharply propagation of the misfit rearrangement to the AlGaInN thin film deposited on the top face, and formation of a quality AlGaInN thin film is possible for it.

[0013] Furthermore, according to the production approach of an AlGaInN thin film according to claim 2, there are the following additional operations.

[0014] Since distorted AlGaInN superlattice is arranged in advance of formation of an AlGaInN thin film, and the movement component to field inboard becomes large by distorted AlGaInN superlattice, a misfit rearrangement can control the propagation to a top face efficiently, and the formation of a quality AlGaInN thin film of it is attained.

[0015] Moreover, according to this invention, formation of an AlGaInN thin film quality also on easy substrates of processing, such as SiC, is possible.

[0016] Furthermore, since high-speed rotation of the substrate was carried out, it can grow up at low temperature comparatively. Control of the gas convection current by the high thing and the control of dissociation of In of growth temperature are attained. Therefore, formation of a quality AlGaInN thin film or AlGaInN multilayers is attained from the former at low temperature.

[0017]

[Example] Hereafter, an example explains this invention. In addition, about the same part, the same sign is described below.

[0018] The MOVPE equipment roughly shown in drawing 1 was used for manufacture of an AlGaInN thin film. Here, the gas installation tubing 2 made from a quartz is attached in the interior of the coil 1 made from a quartz. It has structure which can supply the raw material containing the raw material containing an III group configuration element, and nitrogen to coincidence from gas installation tubing made from a quartz. The coil 3 for high-frequency heating is installed in the periphery of the coil 1 made from a quartz, and the susceptor 4 made from graphite by which the SiC coat was carried out is installed in the interior. The susceptor 4 made from graphite is supported by the motor by the susceptor bearing bar 5 pivotable to 1000 revolution-per-minute extent. It has the composition that the substrate 7 carried on the tray 6 made from a quartz can be installed in susceptor 4 made from graphite top face. Moreover, the exhaust port 8 connected to the vacuum pump is established in the pars basilaris ossis occipitalis of the coil 1 made from a quartz, and the pressure regulation in the coil 1 made from a quartz and exhaust air of gas can be performed.

[0019] (Example 1) Cross-section structural drawing of the AlGaInN thin film produced to drawing 2 by the formation approach of the Al_xGa_yIn_zN thin film (AlGaInN is called $x+y+z=1$, $0 \leq x \leq 1$, $0 \leq y \leq 1$, $0 \leq z \leq 1$, and the following.) of the first example of this invention is shown. About the formation approach of the AlGaInN thin film using the MOVPE equipment of drawing 1, order is explained later on.

[0020] After carrying out cleaning washing of the 6 H-SiC substrate 11, it has arranged as a crystal growth substrate on the tray 6 made from a quartz, and introduced in the coil 1 made from a quartz. After introducing hydrogen gas in the coil 1 made from a quartz and setting coil 1 made from a quartz internal pressure as 1/10 atmospheric pressure, the susceptor 4 made from graphite was rotated by 1000 revolutions per minute. Subsequently, the temperature up of the susceptor 4 made from graphite was carried out to 1100 degrees C in hydrogen gas, and 6 H-SiC substrate 11 front face was defecated.

[0021] Then, after lowering substrate temperature to 900 degrees C and introducing ammonia gas as a V group raw material on the 11th page of 6 H-SiC substrate from the gas installation tubing 2 made from a quartz, after 10 seconds, trimethylaluminum was supplied as an III group raw material, and the single crystal AlN layer 12 of 10nm of thickness was deposited. Since this AlN layer 12 is about 10nm, it serves as film of high quality into which a defect does not go. Moreover, this layer also has ***** which improves the concordance of the layer and SiC substrate which are made to deposit from now on. Although an AlGaInN layer and the lattice constant of a SiC substrate are near, it is because there is a difference in a configuration element, like aluminum is not included.

[0022] Then, after suspending supply of trimethylaluminum and lowering substrate temperature to 600 degrees C, trimethylaluminum was again supplied as an III group raw material from the gas installation tubing 2 made from a quartz, and the non-single crystal AlN layer 13 of 20nm of thickness was deposited. This was used as a buffer coat. Although the AlN layer 12 is less than critical thickness, and a defect does not enter since thickness is also thin, this AlN13 serves as a non-single crystal. It means that a non-single crystal is not a perfect single crystal here, and polycrystal and an

amorphous substance are also contained.

[0023] Subsequently, after carrying out the temperature up of the substrate temperature to 1000 degrees C, trimethylaluminum and trimethylgallium were supplied as an III group raw material, and the AlGaIn layer 14 of 3 micrometers of thickness was deposited. A presentation is aluminum_{0.1}Ga_{0.9}N. AlGaIn layer 14 front face became flat with growth of 3 micrometers.

[0024] Furthermore, after lowering substrate temperature at 900 degrees C, trimethylgallium, trimethylaluminum, and trimethylindium were supplied to coincidence and the AlGaInN layer 15 of 3 micrometers of thickness was deposited. A presentation is aluminum_{0.8}Ga_{0.05}In_{0.15}N.

[0025] After suspending supply of trimethylgallium, trimethylaluminum, and trimethylindium finally, supply of ammonia was suspended in the place which lowered substrate temperature and became the temperature of 300 degrees C or less. After dropping the temperature of a substrate to a room temperature, the substrate was taken out from the inside of the coil 1 made from a quartz.

[0026] In this example, in spite of having deposited the thick film 6 micrometers or more on the substrate, there was also no generating of a crack, it was surface flatness, and as for carrier concentration, according to the hall effect, 10^{15}cm^{-3} and a 4 yuan mixed-crystal layer with very few defects were obtained.

[0027] Moreover, when rotating the susceptor 4 made from graphite by 10 revolutions per minute, it checked that a crystal front face is uneven. In presentation of 4 yuan was set to 0.15 to In presentation of a mixed-crystal layer having been 0.06 in the case of this example, In was incorporated by high-speed rotation of 1000 revolutions per minute, and a rate increased.

[0028] According to this example, compared with the AlGaInN layer deposited only through the non-single crystal layer on conventional silicon on sapphire, propagation of the defect generated from the buffer coat interface was reduced remarkably.

[0029] Thus, the reason which can deposit a very quality AlGaInN layer on a substrate is that, as for the non-single crystal AlN layer 13, dispersion in thickness or the crystal structure can deposit few layers since the SiC substrate 11 with a near lattice constant was used for the AlGaInN layer 15 upwards and the thin single crystal AlN layer 12 which is the same configuration element as the non-single crystal AlN layer 13 was deposited on this substrate 11. If an AlGaInN layer is grown up through this single crystal AlN layer 12 and the non-single crystal layer 13, it is not necessary to necessarily use a SiC substrate. however, a SiC substrate is markedly boiled compared with silicon on sapphire, and is easy handling.

[0030] Moreover, although the single crystal AlN layer 12 and the non-single crystal AlN layer 13 which a presentation becomes from AlN are used on the SiC substrate here, Ga may be contained in this presentation and you may be the so-called $\text{Al}_x\text{Ga}_{1-x}\text{N}$ layer ($0 < x < 1$).

[0031] In addition, although aluminum_{0.1}Ga_{0.9}N layer 14 is used on the non-single crystal AlN layer 13 in this example for growth of the quality AlGaInN layer 15, you may be the case where this layer does not exist.

[0032] (Example 2) Cross-section structural drawing of the AlGaInN thin film produced by the formation approach of the AlGaInN thin film of the second example of this invention to drawing 3 is shown. The difference from an example 1 is using the AlGaIn/GaInN strained layer superlattice 18 between the AlGaInN layer 15 and the AlGaIn layer 14. About the manufacture approach of the AlGaInN thin film using the MOVPE equipment of drawing 1, order is explained later on.

[0033] After carrying out cleaning washing of the 6 H-SiC substrate 11, it has arranged as a crystal growth substrate on the tray 6 made from a quartz, and introduced in the coil 1 made from a quartz. After introducing hydrogen gas in the coil 1 made from a quartz and setting coil 1 made from a quartz internal pressure as 1/10 atmospheric pressure, the susceptor 4 made from graphite was rotated by 1000 revolutions per minute. Subsequently, the temperature up of the susceptor 4 made from graphite was carried out to 1100 degrees C in hydrogen gas, and 6 H-SiC substrate 11 front face was defecated.

[0034] Then, after lowering substrate temperature to 900 degrees C and introducing ammonia gas as a V group raw material on the 11th page of 6 H-SiC substrate from the gas installation tubing 2 made from a quartz, after 10 seconds, trimethylaluminum was supplied as an III group raw material, and the single crystal AlN layer 12 of 10nm of thickness was deposited.

[0035] Then, after suspending supply of trimethylaluminum and lowering substrate temperature to 600 degrees C, trimethylaluminum was again supplied as an III group raw material from the gas installation tubing 2 made from a quartz, and the non-single crystal AlN layer 13 of 20nm of thickness was deposited. This was used as a buffer coat.

[0036] Subsequently, after carrying out the temperature up of the substrate temperature to 1000 degrees C, trimethylaluminum and trimethylgallium were supplied as an III group raw material, and the AlGaIn layer 14 of 3 micrometers of thickness was deposited. A presentation is aluminum_{0.1}Ga_{0.9}N. AlGaIn layer 14 front face became flat with growth of 3 micrometers.

[0037] Then, after lowering substrate temperature at 900 degrees C, trimethylgallium, trimethylaluminum, and trimethylindium were supplied, the AlGaIn layer 16 of 2nm of thickness and the GaInN layer 17 of 2nm of thickness were deposited 40 periods continuously, and the AlGaIn/AlInN strained layer superlattice 18 was formed. Presentations are aluminum_{0.9}Ga_{0.1}N and aluminum_{0.7}In_{0.3}N.

[0038] Furthermore, trimethylgallium, trimethylaluminum, and trimethylindium were supplied to coincidence and the AlGaInN layer 15 of 3 micrometers of thickness was deposited. A presentation is aluminum_{0.8}Ga_{0.05}In_{0.15}N.

[0039] After suspending supply of trimethylgallium, trimethylaluminum, and trimethylindium finally, supply of ammonia was suspended in the place which lowered substrate temperature and became the temperature of 300 degrees C or less. After dropping the temperature of a substrate to a room temperature, the substrate was taken out from the inside of the coil 1

made from a quartz.

[0040] In this example, in spite of having deposited the thick film 6 micrometers or more on the substrate, there was also no generating of a crack, it was surface flatness, and as for carrier concentration, according to the hall effect, 10^{15}cm^{-3} and a 4 μm mixed-crystal layer with very few defects were obtained.

[0041] Moreover, when rotating the susceptor 4 made from graphite by 10 revolutions per minute, it checked that a crystal front face is uneven. In presentation of 4 μm was set to 0.15 to In presentation of a mixed-crystal layer having been 0.06 in the case of this example, In was incorporated by high-speed rotation of 1000 revolutions per minute, and a rate increased.

[0042] Since propagation of the defect generated from the buffer coat interface was not only reduced remarkably, but had arranged the strained layer superlattice 18 compared with the AlGaInN layer deposited only through the non-single crystal layer on conventional silicon on sapphire according to this example, it could control efficiently that a misfit rearrangement spread from the AlGaN layer 14 to a top face, and about double [more] figures were reduced compared with the case of an example 1 in the defect density of the AlGaInN layer 15.

[0043] When silicon on sapphire was used for this formation approach, effectiveness was not accepted but, in the case of the SiC substrate, was completely very effective.

[0044] In addition, this invention is not limited to the example mentioned above. Moreover, the substrate to be used is not limited to an above-mentioned substrate. however, a SiC substrate and a ZnO substrate have the difference of a lattice constant with an AlGaInN layer alike and smaller than silicon on sapphire, and are easy also handling. Neither the raw material used for crystal growth nor a thin film presentation is also above-mentioned limitations. A presentation or configuration of AlGaInN multilayers are not limited, either.

[0045] Furthermore, it cannot be overemphasized that it is applicable also to the multilayered film formation as a light emitting device using this invention.

[0046]

[Effect of the Invention] Thus, according to this invention, if an AlGaN single crystal thin film is formed after forming the non-single crystal AlN on a single crystal AlN thin film and easing grid distortion, generating of a defect will be controlled, and since propagation of the rearrangement to the AlGaInN thin film deposited on the top face is considered as the configuration which can be reduced sharply, a quality AlGaInN thin film can be formed.

[0047] Moreover, since distorted AlGaInN superlattice is arranged in advance of formation of an AlGaInN thin film, since the movement component to field inboard becomes large, the rearrangement generated from the substrate or the buffer coat interface can control the propagation to a top face efficiently, and can form a quality AlGaInN thin film.

[0048] Therefore, it is very useful to the blue semiconductor laser component manufacture which can be used for high blue light emitting diode, the light source for information processors, etc. of luminous efficiency.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The schematic diagram of the MOVPE equipment explaining the formation approach of the example of this invention

[Drawing 2] Cross-section structural drawing of the AlGaInN thin film by the formation approach of the AlGaInN thin film of the first example of this invention

[Drawing 3] Cross-section structural drawing of the AlGaInN layer membrane by the formation approach of the AlGaInN layer membrane of the second example of this invention

[Description of Notations]

- 1 Coil made from Quartz
- 2 Gas Installation Tubing made from Quartz
- 3 Coil for High-frequency Heating
- 4 Susceptor made from Graphite
- 5 Susceptor Bearing Bar
- 6 Tray made from Quartz
- 7 Substrate
- 8 Exhaust Port
- 11 6 H-SiC Substrate
- 12 Single Crystal AlN Layer
- 13 Non-Single Crystal AlN Layer
- 14 AlGaIn Layer
- 15 AlGaInN Layer
- 16 AlGaIn Layer
- 17 GaInN Layer
- 18 AlGaIn/AlInN Strained Layer Superlattice

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(71)出願人 000005821

松下電器産業株式会社

大阪府門真市大字門真1006番地

(72)発明者 萬濃 正也

大阪府門真市大字門真1006番地 松下電器
産業株式会社内

(72)発明者 大仲 清司

大阪府門真市大字門真1006番地 松下電器
産業株式会社内

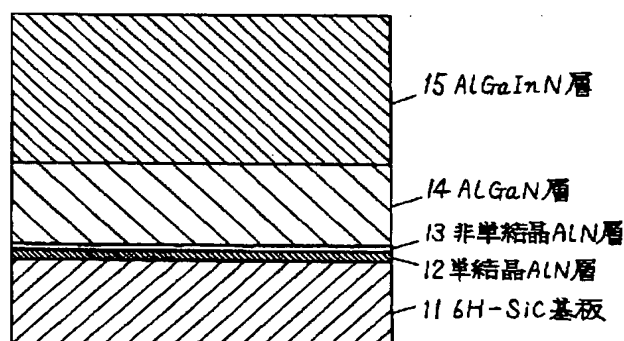
(74)代理人 弁理士 小鍛冶 明 (外2名)

(54)【発明の名称】 半導体薄膜及び半導体薄膜の製造方法

(57)【要約】

【目的】 青色発光ダイオード等に用いることのできる青色半導体レーザ素子製造に適した、転位や点欠陥の少ない高品質なAlGaInN薄膜の形成方法を提供する。

【構成】 加熱されたSiC基板表面上にIII族構成元素を含む原料および窒素を含む原料を供給して緩衝層を介してAlGaInN薄膜を形成する方法である。まず、800℃に加熱したSiC基板11上に単結晶AlN12を形成する。そして、600℃で20nmの非単結晶AlN13を形成する。次いで、900℃以上の基板温度で単結晶AlGaN層14を形成する。そしてAlGaN層14上に格子整合するAlGaInN層15を形成する。これにより転位や点欠陥の発生を抑制し、高品質なAlGaInN薄膜を形成できる。



【特許請求の範囲】

【請求項1】加熱された基板表面上にIII族構成元素を含む原料および窒素を含む原料を供給して緩衝層を介してAlGaInN薄膜を形成する方法であって、前記基板上に第一のAlGaInN単結晶薄膜を形成した後に、AlGaInNからなる緩衝層を形成する工程と、次いで第二のAlGaInN単結晶薄膜を形成した後に、AlGaInN単結晶薄膜を形成する工程と、を含むことを特徴とするAlGaInN半導体薄膜の製造方法。

【請求項2】加熱された基板表面上にIII族構成元素を含む原料および窒素を含む原料を供給して緩衝層を介してAlGaInN薄膜を形成する方法であって、前記基板上に第一のAlGaInN単結晶薄膜を形成した後に、AlGaInNからなる緩衝層を形成する工程と、次いで第二のAlGaInN単結晶薄膜を形成した後に、前記第二のAlGaInN単結晶薄膜中もしくは前記第二のAlGaInN単結晶薄膜上に、複数の組成の異なるAlGaInN層からなる歪超格子構造を形成する工程と、を含むことを特徴とするAlGaInN半導体薄膜の製造方法。

【請求項3】第一、及び第二のAlGaInN単結晶薄膜は、800℃以上の基板温度で形成し、AlGaInNからなる緩衝層は800℃以下の基板温度で形成することを特徴とする請求項第1または2に記載のAlGaInN半導体薄膜の製造方法。

【請求項4】形成する方法が有機金属を用いた気相成長法であって、基板を配置した加熱体の回転速度を300回転/分以上とすることを特徴とする請求項1または2に記載のAlGaInN半導体薄膜の製造方法。

【請求項5】基板がSiCまたはZnOであることを特徴とする請求項1または2に記載のAlGaInN半導体薄膜の製造方法。

【請求項6】単結晶AlGaIn層と、前記単結晶AlGaIn層上に形成したAlGaInからなる緩衝層と、前記AlGaInからなる緩衝層上に形成したAlGaIn層と、を備えたことを特徴とする半導体薄膜構造。

【請求項7】SiC基板またはZnO基板上に、請求項6に記載の半導体薄膜構造を堆積したことを特徴とする半導体発光素子。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、緑・青色発光ダイオードや光ディスク等情報処理装置用光源に用いることのできる青色もしくは更に短波長の半導体レーザ素子の製造方法に関するもので、特に窒化物系材料の薄膜形成に係わるものである。

【0002】

【従来の技術】1988年に670nm帯AlGaInP系赤色半導体レーザが商品化されて以来、レーザプリ

ンター、光ディスク等の情報処理装置用光源として短波長半導体レーザの開発が活発に行われている。当初670～690nmが開発の中心であったが、バーコードリーダーの視認性の改善、光ディスクの高密度化等の要求にともなって、波長領域はHe-Neガスレーザと同レベルの630nm帯へと移行しつつある。さらに将来、記憶容量の増大に伴って、赤色よりさらに短波長の青・緑色から紫外域にわたる半導体レーザの実現が切望されており、p型導電型制御が可能となったことを契機にII-VI族系半導体レーザの研究が急速に進展してきている。一方、窒化ガリウム(GaN)は、約3.4eVの広エネルギーギャップを持つ直接遷移型の化合物半導体で青色から紫外領域にわたる発光素子として有望な材料であるがGaNバルク基板結晶が容易に作製できず、また、ほかに適当な基板結晶がないことから半導体レーザとしての開発はあまり進展していなかった。

【0003】GaN薄膜の作製方法としては、 α -Al₂O₃ (サファイア) 基板上にMOVPE法(有機金属気相成長法)により気相成長する方法が一般的に用いられている。これは、例えばトリメチルガリウムとアンモニアを1050℃程度に加熱した基板、例えば、サファイア基板の表面上で分解、反応させ、GaN薄膜を成長しようとするものである。最近サファイアの(0001)C面を用い、低温で堆積したGaNやAlN緩衝層を介して比較的良質のGaN薄膜を形成できることが実証され、青色発光ダイオードとして商品化されまでに至った。

【0004】

【発明が解決しようとする課題】上述の従来技術によれば、サファイアC面とGaNとの間には13.8%という極めて大きな格子不整合や大きな熱膨張係数の差があるため、成長した窒化膜にはピットやクラックが入りやすく、均一で平坦性のよい窒化膜の成長が困難であった。

【0005】低温で堆積した緩衝層を介した場合においては、格子不整合の緩和は効率的におこり平坦で鏡面性の窒化膜の成長が可能であるが、依然として10⁸cm⁻²以上のミスフィット転位が存在し高品質な薄膜の形成が困難であった。さらに従来技術によれば、サファイアが基板として用いられていたため加工が困難でデバイスの作製が容易でないという問題があった。

【0006】本発明は、転位が少なく平坦性のよいAlGaInN薄膜の形成方法を提供することを目的とする。同時に、加工の容易な基板上への高品質なAlGaInN薄膜の形成方法を提供することを目的とする。

【0007】

【課題を解決するための手段】上記目的を達成するために、請求項1記載のAlGaInN薄膜の形成方法は、加熱された基板表面上にIII族構成元素を含む原料および窒素を含む原料を供給して緩衝層を介してAlGaIn

nN薄膜を形成する方法において、前記基板上に第一のAlGaIn単結晶薄膜を形成した後にAlGaInからなる緩衝層を形成する工程と、次いで第二のAlGaIn単結晶薄膜を形成した後にAlGaInN単結晶薄膜を形成する工程を少なくとも含むことを特徴とする。ここで、前記第一及び第二のAlGaIn単結晶薄膜は800℃以上の基板温度で形成し、前記AlGaInからなる緩衝層は800℃以下の基板温度とすることが望ましい。

【0008】請求項2記載のAlGaInN薄膜の形成方法は、加熱された基板表面上にIII族構成元素を含む原料および窒素を含む原料を供給して緩衝層を介してAlGaInN薄膜を形成する方法において、前記基板上に第一のAlGaIn単結晶薄膜を形成した後にAlGaInからなる緩衝層を形成する工程と、次いで第二のAlGaIn単結晶薄膜を形成した後にAlGaInN単結晶薄膜を形成する工程と、前記第二のAlGaIn単結晶薄膜もしくは前記第二のAlGaIn単結晶薄膜上に複数の組成の異なるAlGaInN層からなる歪超格子構造を形成する工程とを少なくとも含むことを特徴とする。ここで、前記第一及び第二のAlGaIn単結晶薄膜は800℃以上の基板温度で形成し、前記AlGaInからなる緩衝層は800℃以下の基板温度とすることが望ましい。

【0009】以上の請求項において、基板を配置した加熱体の回転速度は300回転/分以上とすること、基板はSiCやZnOであることが望ましい。

【0010】

【作用】請求項1のAlGaInN薄膜の作製方法によれば、以下のような作用がある。

【0011】AlGaInNとの格子不整合差や熱膨張係数差がサファイア基板と比べ極めて小さいSiC、ZnO基板を用いることによって、臨界膜厚以下であれば単結晶AlN薄膜を平坦かつ均一に堆積できる。このAlN薄膜上に低温で堆積する非単結晶AlNは同一元素からなる単結晶上に堆積するので、その表面は平坦かつ均一とすることが可能となる。

【0012】さらには、単結晶層を介して非単結晶緩衝層を低温で堆積しているため、基板からの不純物拡散は著しく低減できる。従って、従来のサファイア基板上に非単結晶緩衝層のみを介して堆積したAlGaInN層に比べ、緩衝層界面から発生した欠陥の伝搬は著しく低減され、上面に堆積したAlGaInN薄膜へのミスフィット転位の伝搬を大幅に低減でき高品質なAlGaInN薄膜の形成が可能である。

【0013】更に、請求項2記載のAlGaInN薄膜の作製方法によれば、以下のような付加的な作用がある。

【0014】AlGaInN薄膜の形成に先立ち歪AlGaInN超格子を配置するので、ミスフィット転位は歪AlGaInN超格子によって面内方向への運動成分

が大きくなるため、上面への伝搬を効率的に抑制でき高品質なAlGaInN薄膜の形成が可能となる。

【0015】また、本発明によれば、SiCなどの加工の容易な基板上にも高品質なAlGaInN薄膜の形成が可能である。

【0016】さらには、基板を高速回転させたので、比較的低温で成長可能であり、成長温度が高いことによるガス対流の抑制、Inの解離の抑制が可能となる。よって従来よりも低温で高品質なAlGaInN薄膜もしくはAlGaInN多層膜の形成が可能となる。

【0017】

【実施例】以下、実施例で本発明を説明する。なお、以下同一部分については同一符号を記す。

【0018】AlGaInN薄膜の製造には、図1に概略的に示すMOVPE装置を用いた。ここで、石英製反応管1の内部には石英製ガス導入管2が取り付けられている。石英製ガス導入管からはIII族構成元素を含む原料および窒素を含む原料を同時に供給できる構成となっている。石英製反応管1の外周には高周波加熱用コイル3が設置され、また、内部にはSiCコートされたグラファイト製サセプター4が設置されている。グラファイト製サセプター4はモーターによって1000回転/分程度に回転可能なサセプター支持棒5により支持されている。グラファイト製サセプター4上面には、石英製トレー6上に搭載された基板7が設置できる構成となっている。また、石英製反応管1の底部には真空ポンプに接続された排気口8が設けられていて、石英製反応管1内の圧力調整及びガスの排気ができる。

【0019】（実施例1）図2に本発明の第一の実施例のAl_xGa_yIn_zN薄膜（ $x+y+z=1$ 、 $0 \leq x \leq 1$ 、 $0 \leq y \leq 1$ 、 $0 \leq z \leq 1$ 、以下、AlGaInNと称す。）の形成方法により作製したAlGaInN薄膜の断面構造図を示す。図1のMOVPE装置を用いたAlGaInN薄膜の形成方法について、順を追って説明する。

【0020】6H-SiC基板11を脱脂洗浄した後、石英製トレー6上に結晶成長基板として配置し、石英製反応管1内に導入した。石英製反応管1内に水素ガスを導入し、石英製反応管1内圧力を1/10気圧に設定した後、グラファイト製サセプター4を1000回転/分で回転させた。次いで、水素ガス中でグラファイト製サセプター4を1100℃まで昇温し、6H-SiC基板11表面の清浄化を行った。

【0021】その後、基板温度を900℃まで降温し、石英製ガス導入管2から6H-SiC基板11面上にV族原料としてアンモニアガスを導入した後、10秒後にIII族原料としてトリメチルアルミニウムを供給して膜厚10nmの単結晶AlN層12を堆積した。このAlN層12は10nm程度であるため、欠陥が入ることのない高品質の膜となっている。またこの層は、これから

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堆積させる層とSiC基板とのなじみをよくするはたらしきもある。SiC基板はAlGaInN層と格子定数は近いが、Alを含んでいないなどの構成元素のちがいがあからである。

【0022】その後、トリメチルアルミニウムの供給を一旦停止し、基板温度を600℃まで降温した後、石英製ガス導入管2からIII族原料としてトリメチルアルミニウムを再度供給して膜厚20nmの非単結晶AlN層13を堆積した。これを緩衝層として用いた。AlN層12は臨界膜厚以内であって、膜厚もうすいため、欠陥がはいることはないが、このAlN13は非単結晶となっている。ここで非単結晶とは、完全な単結晶ではないことを意味し、多結晶や非晶質も含まれる。

【0023】次いで、基板温度を1000℃に昇温した後、III族原料としてトリメチルアルミニウムとトリメチルガリウムを供給して膜厚3μmのAlGaInN層14を堆積した。組成は、Al_{0.1}Ga_{0.9}Nである。3μmの成長によってAlGaInN層14表面は平坦となった。

【0024】更に、基板温度を900℃に降温した後、トリメチルガリウム、トリメチルアルミニウムとトリメチルインジウムを同時に供給して膜厚3μmのAlGaInN層15を堆積した。組成はAl_{0.8}Ga_{0.05}In_{0.15}Nである。

【0025】最後にトリメチルガリウム、トリメチルアルミニウムとトリメチルインジウムの供給を停止した後、基板温度を降温して300℃以下の温度になったところでアンモニアの供給を停止した。基板の温度を室温まで降下させた後、石英製反応管1内より基板を取り出した。

【0026】本実施例においては、基板上に6μm以上の厚膜を堆積したにもかかわらず、クラックの発生もなく表面平坦であり、ホール効果によるとキャリア濃度は 10^{16} cm^{-3} と極めて欠陥の少ない四元混晶層が得られた。

【0027】また、グラファイト製サセプター4を10回転/分で回転させた場合は、結晶表面は凸凹で四元混晶層のIn組成が0.06であったのに対し、本実施例の場合、In組成は0.15となり、1000回転/分の高速回転によりInの取り込まれ率が增大することを確認した。

【0028】本実施例によれば、従来のサファイア基板上に非単結晶層のみを介して堆積したAlGaInN層に比べ、緩衝層界面から発生した欠陥の伝搬は著しく低減された。

【0029】このように基板上に非常に品質のよいAlGaInN層を堆積できる理由は、AlGaInN層15に格子定数の近いSiC基板11を用いた上に、この基板11上に、非単結晶AlN層13と同じ構成元素であるうすい単結晶AlN層12を堆積したので、非単結晶AlN層13は厚みや結晶構造のばらつきが少ない層

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を堆積できるからである。この単結晶AlN層12と非単結晶層13とを介してAlGaInN層を成長させれば、かならずしもSiC基板を用いなくてもよい。ただ、SiC基板はサファイア基板に比べて格段に取扱が容易である。

【0030】またここではSiC基板上に組成がAlNからなる単結晶AlN層12および非単結晶AlN層13を用いているが、この組成にGaが含まれていてもよく、いわゆるAl_xGa_{1-x}N層(0≤x≤1)であって

【0031】なお、本実施例では、品質のよいAlGaInN層15の成長のために、非単結晶AlN層13の上に、Al_{0.1}Ga_{0.9}N層14を用いているが、この層がない場合であってもかまわない。

【0032】(実施例2) 図3に本発明の第二の実施例のAlGaInN薄膜の形成方法により作製したAlGaInN薄膜の断面構造図を示す。実施例1との違いは、AlGaInN層15とAlGaInN層14との間にAlGaInN/GaInN歪超格子18を用いていることである。図1のMOVPE装置を用いたAlGaInN薄膜の製造方法について、順を追って説明する。

【0033】6H-SiC基板11を脱脂洗浄した後、石英製トレー6上に結晶成長基板として配置し、石英製反応管1内に導入した。石英製反応管1内に水素ガスを導入し、石英製反応管1内圧力を1/10気圧に設定した後、グラファイト製サセプター4を1000回転/分で回転させた。次いで、水素ガス中でグラファイト製サセプター4を1100℃まで昇温し、6H-SiC基板11表面の清浄化を行った。

【0034】その後、基板温度を900℃まで降温し、石英製ガス導入管2から6H-SiC基板11面上にV族原料としてアンモニアガスを導入した後、10秒後にIII族原料としてトリメチルアルミニウムを供給して膜厚10nmの単結晶AlN層12を堆積した。

【0035】その後、トリメチルアルミニウムの供給を一旦停止し、基板温度を600℃まで降温した後、石英製ガス導入管2からIII族原料としてトリメチルアルミニウムを再度供給して膜厚20nmの非単結晶AlN層13を堆積した。これを緩衝層として用いた。

【0036】次いで、基板温度を1000℃に昇温した後、III族原料としてトリメチルアルミニウムとトリメチルガリウムを供給して膜厚3μmのAlGaInN層14を堆積した。組成はAl_{0.1}Ga_{0.9}Nである。3μmの成長によってAlGaInN層14表面は平坦となった。

【0037】その後、基板温度を900℃に降温した後、トリメチルガリウム、トリメチルアルミニウムとトリメチルインジウムを供給して膜厚2nmのAlGaInN層16と膜厚2nmのGaInN層17を連続して40周期堆積し、AlGaInN/AlInN歪超格子18を形成した。組成はAl_{0.9}Ga_{0.1}N、Al_{0.7}In_{0.3}Nで

ある。

【0038】更に、トリメチルガリウム、トリメチルアルミニウムとトリメチルインジウムを同時に供給して膜厚 $3\mu\text{m}$ の AlGaInN 層15を堆積した。組成は $\text{Al}_{0.8}\text{Ga}_{0.05}\text{In}_{0.15}\text{N}$ である。

【0039】最後にトリメチルガリウム、トリメチルアルミニウムとトリメチルインジウムの供給を停止した後、基板温度を降温し 300°C 以下の温度になったところでアンモニアの供給を停止した。基板の温度を室温まで降下させた後、石英製反応管1内より基板を取り出した。

【0040】本実施例においては、基板上に $6\mu\text{m}$ 以上の厚膜を堆積したにもかかわらず、クラックの発生もなく表面平坦であり、ホール効果によるとキャリア濃度は 10^{16}cm^{-3} と極めて欠陥の少ない四元混晶層が得られた。

【0041】また、グラファイト製サセプター4を10回転/分で回転させた場合は、結晶表面は凸凹で四元混晶層の In 組成が0.06であったのに対し、本実施例の場合、 In 組成は0.15となり、1000回転/分の高速回転により In の取り込まれ率が增大することを確認した。

【0042】本実施例によれば、従来のサファイア基板上に非単結晶層のみを介して堆積した AlGaInN 層に比べ、緩衝層界面から発生した欠陥の伝搬は著しく低減されただけでなく、歪超格子18を配置したので、ミスフィット転位が AlGaInN 層14から上面へ伝搬するのを効率的に抑制でき、 AlGaInN 層15の欠陥密度を実施例1の場合に比べてさらに2桁程度が低減された。

【0043】この形成方法は、サファイア基板を用いた場合には全く効果は認められず、 SiC 基板の場合に極めて有効であった。

【0044】なお、本発明は上述した実施例に限定されるものではない。また、用いる基板は上述の基板には限定されない。ただ、 SiC 基板や ZnO 基板は、 AlGaInN 層との格子定数の差がサファイア基板よりも格段に小さく、また取扱も容易である。結晶成長に用いた原料や薄膜組成も上述の限りではない。 AlGaInN 多層膜の組成や構成も限定されるものでない。

【0045】さらには、本発明を用いた発光素子として

の多層薄膜形成にも適用できるのは言うまでもない。

【0046】

【発明の効果】このように本発明によれば、単結晶 AlN 薄膜上に非単結晶 AlN を形成し格子歪みを緩和した後に AlGaInN 単結晶薄膜を形成すると欠陥の発生が抑制され、上面に堆積した AlGaInN 薄膜への転位の伝搬を大幅に低減できる構成とするため、高品質な AlGaInN 薄膜を形成できる。

【0047】また、 AlGaInN 薄膜の形成に先立ち歪 AlGaInN 超格子を配置するので、基板や緩衝層界面から発生した転位は面内方向への運動成分が大きくなるため、上面への伝搬を効率的に抑制でき高品質な AlGaInN 薄膜を形成できる。

【0048】したがって、発光効率の高い青色発光ダイオードや情報処理装置用光源などに用いることのできる青色半導体レーザ素子製造に極めて有用である。

【図面の簡単な説明】

【図1】本発明の実施例の形成方法を説明するMOVPE装置の概略図

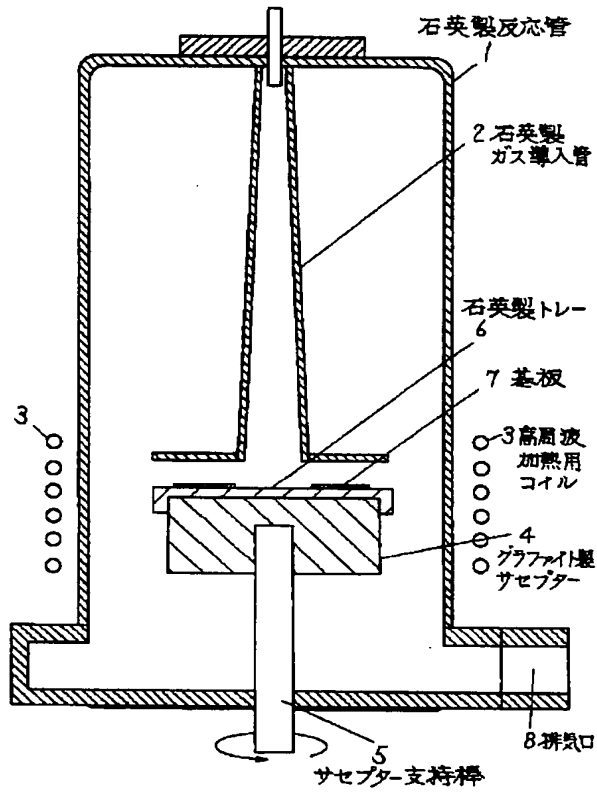
【図2】本発明の第一の実施例の AlGaInN 薄膜の形成方法による AlGaInN 薄膜の断面構造図

【図3】本発明の第二の実施例の AlGaInN 層膜の形成方法による AlGaInN 層膜の断面構造図

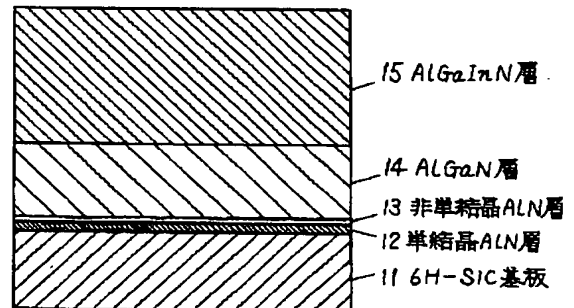
【符号の説明】

- 1 石英製反応管
- 2 石英製ガス導入管
- 3 高周波加熱用コイル
- 4 グラファイト製サセプター
- 5 サセプター支持棒
- 6 石英製トレイ
- 7 基板
- 8 排気口
- 11 6H-SiC 基板
- 12 単結晶 AlN 層
- 13 非単結晶 AlN 層
- 14 AlGaInN 層
- 15 AlGaInN 層
- 16 AlGaInN 層
- 17 GaInN 層
- 18 $\text{AlGaInN}/\text{AlInN}$ 歪超格子

【図1】



【図2】



【図3】

